

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL MEMORANDUM 1339

VELOCITY OF ACTION OF OXYGEN, HYDROGEN SULFIDE,
AND HALOGENS ON METALS

By G. Tammann and W. Köster

Translation

“Die Geschwindigkeit der Einwirkung von Sauerstoff,
Schwefelwasserstoff, und Halogenen auf
Metalle.” Zeitschrift für anorg. und
allg. Chemie, vol. 123, August 1922.



Washington

June 1952



3 1176 01440 4637

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

TECHNICAL MEMORANDUM 1339

VELOCITY OF ACTION OF OXYGEN, HYDROGEN SULFIDE, AND

HALOGENS ON METALS*

By G. Tammann and W. Köster

If iodine, chlorine, or air act on a metal at a high temperature, the metal often takes on colors. At first, the metal is light yellow, then brownish yellow, orange, red, purple, violet, indigo, sky blue, and so forth. It is often possible to distinguish as many as 60 different colors; after the appearance of a grayish-red color (red of the fourth order), the distinction in the subsequent colors becomes uncertain. These colors arise from the interference in the reflections at the surfaces of the metal and its reaction products; certain colors of the incident white light are destroyed and the rest combine into the previously mentioned mixed colors. To each color there corresponds a layer of definite thickness; and there are tables which, for definite colors, give the thickness of the corresponding air layers. When this thickness is divided by the index of refraction of the formed reaction product, the thickness layer is obtained in micromicrons ($\mu\mu = 1 \times 10^{-6}$ mm). As an illustration, the following colors correspond to the different layer thicknesses of silver iodide:

	Thickness ($\mu\mu$) Molecules AgI	
Straw yellow	61	43
Red I	108	77
Red II	216	155
Red III	330	235
Red IV	439	313

Since from red I to red IV it is possible to distinguish about 60 colors without difficulty, an increase in thickness of the layer by

*"Die Geschwindigkeit der Einwirkung von Sauerstoff, Schwefelwasserstoff, und Halogenen auf Metalle." Zeitschrift für anorg. und allg. Chemie, vol. 123, August 1922, pp. 196-201 and 208-224.

about 4.5 molecules can be clearly distinguished with the naked eye. By spectral decomposition of the reflected light the sensitivity of the method can be considerably raised.

For the case of Ag, Cu, and Pb in iodine-containing air, it is shown in reference 1 that the thicknesses y of the iodine layers, for constant concentration of the iodine in the air, vary with time according to the law

$$y^2 = 2pt \quad (1)$$

or the rate of increase in thickness is

$$\frac{dy}{dt} = \frac{p}{y} \quad (2)$$

where p is a constant which is determined by the product of the concentration drop of the iodine in the layer of the reaction product and the corresponding diffusion coefficient.

A further investigation, particularly of the oxidation velocity of metals, showed that for an oxide coating on a metal the increase in thickness is determined by a different law from that for the metal in iodine-containing air. This law is

$$t = ae^{by} - a \quad (3)$$

and

$$\frac{dy}{dt} = \frac{1}{ab} e^{-by} \quad (4)$$

In these equations, a denotes a constant which is independent of the temperature. The constant b determines the retardation in the thickening of the oxide coating with increasing time t , and, in turn, is an exponential function of the temperature. At the start of the reaction, the initial velocity is obtained as

$$\frac{dy}{dt} = \frac{1}{ab} \quad (5)$$

The geometrical meaning of a is as follows. If the logarithms of t are plotted as abscissas and the values of y as ordinates, a straight line, is obtained for each temperature all the lines intersecting the axis of abscissas at the value $\log a$ (fig. 1). If, on the other hand, the values of t are plotted on the axis of abscissas (fig. 2), an exponential curve is obtained for each temperature; these curves intersect each other at the same point. The distance of this point from the origin is equal to a . In figure 1 the values of $\log t$ correspond to the values of t in figure 2, and the values of y are the same in both.

From equation (3) is obtained

$$b = \frac{\ln(t + a) - \ln a}{y}$$

hence in figure 1 with the y -axis b is the tangent of the angle made by one of the straight lines.

Whereas a was found to be independent of the temperature, b varies with the temperature according to an exponential law, namely,

$$b_T = b_{T_0} e^{-c(T-T_0)} \quad (6)$$

Both laws state that the velocity of the chemical reaction indicated by the appearance of the colors is very great. For the rate of thickness increase, it follows from the first law that, at the first instant, in the absence of the layer of the reaction product the velocity is infinitely large (see equation (2)); and from the second law, it follows that although the velocity is not infinitely large, it becomes very large in comparison with the diffusion velocity of the reagent through the layer of the reaction product since in equation (5) a and b are two proper fractions.

The two laws provide the only method of investigating the diffusion in anisotropic media. From the rate of increase in thickness as a function of time, the concentration drop of the reagent in the layer of the reaction product can be derived. Since the reagent reaching the surface of the metal is immediately converted into the reaction product, the concentration c of the reagent at the surface of the metal becomes infinitesimal. In the outer layer of the reaction product, the concentration c of the reagent will have a definite value c_0 , which, however, need not be identical with the concentration of the reagent in the outer adjacent layer of the gas which contains the reagent.

The quantity of reagent diffused at the metal during the time dt is equal to the concentration drop at the surface of the metal multiplied by the diffusion coefficient D . Through reaction with the metal there arises from 1 mole of the reagent per square centimeter a layer of the reaction product of thickness $(M/d)^{1/3}$, where M is the weight of the reaction product which is formed from 1 mole of the reagent and d is the thickness of the reaction product. If D and c_0 are measured in moles, the new layer of the reaction product formed on the metal in time dt will be equal to

$$\frac{dy}{dt} = \left(\frac{M}{d}\right)^{\frac{1}{3}} D \frac{dc_0}{dy} \quad (7)$$

The rate of thickness increase is thus proportional to the concentration drop at the metal surface. If, furthermore,

$$\frac{dc_0}{dy} = \frac{c_0}{y} \quad (8)$$

there is obtained from equations (7) and (8)

$$\frac{dy}{dt} = \left(\frac{M}{d}\right)^{\frac{1}{3}} D \frac{c_0}{y} \quad (9)$$

If c_0 has a constant value, the rate of thickness increase dy/dt is inversely proportional to the layer thickness y , or the layer thickness varies parabolically with the time. The concentration c_0 will be constant only if the reagent has a definite concentration in the gas and if the concentration of the reaction product on the surface remains constant as a result of a sufficiently rapid stream. For this case there is to be expected a strong effect of the concentration of the reagent in the gas and of the velocity or the gas.

From equation (9) the value of the product Dc_0 is obtained from the measurements of y and t but not from the values of the individual factors. The concentration c_0 could be determined only if D is known from other tests. The fact that c_0 may not be set equal to the concentration of the reagent in the gas follows from the observation that silver iodide is colored deeply brown in iodine containing slightly colored air.

Equation (8) corresponds to the fundamental law of hydrodiffusion, which is analogous to that of heat conduction, for a layer of variable thickness in which the concentrations or temperatures have constant values at both surfaces.

Quite a different diffusion law is obtained when the layer thickness of the reaction product depends on the time according to an exponential law of the form of equation (3). In this case the concentration of the diffusing reagent from layer to layer of thickness dy is reduced by amount b , a proper fraction. Whereas it has the value c_0 on the surface, at a depth y it will have the value

$$c = c_0 e^{-by} \quad (10)$$

The value b is identical with the value of b in equation (4), and is therefore to be determined from the observation of the colors; the value c_0 is, however, unknown.

It was found that, for the oxidation of Fe and Ni, the increase in thickness of the oxide layers with time within wide limits is independent of the oxygen content of the acting nitrogen-oxygen mixture. The same must be true for c_0 . Further investigations must be made to clarify this astonishing fact.

Test Setup

It is of considerable importance that the metal plates on which the reagents are to act are of a small mass so that when introduced in the corresponding heater they quickly assume the temperature of the heater. The mass of the plates, which were polished on one side, was correspondingly 70 to 120 milligrams. Through the heater, which consisted of a glass tube 40 centimeters long surrounded by a coil of wire, a gas stream of definite velocity was introduced. After the temperature of the heater, measured by a thermocouple, had become constant, the plate was placed in the heater with the aid of a glass tube which served at the same time as a tube for conducting the gas away. The color of the plate could be easily observed in scattered daylight with the naked eye or with the aid of magnifying device. On introducing the plate, the thermocouple showed a temperature drop by 2 to 4° C; in 1/2 to 1 minute the initial value of the temperature was again reached.

The thicknesses of the layers are given in micromicrons on the basis of the corresponding color of the plate, that is, in thicknesses of air layers which correspond to the color. The basic data are found

in Rollet's table (reference 2). On account of the different natural colors of the metals and of the reaction products, slight deviations in the color tones of the colors given in the Rollet table occur for colors of the first and second orders. Because the color series remain the same, however, the determination and layer thicknesses of the series are not disturbed. The plates after they were polished, were investigated in the hard state, as this rendered the thickening more uniform. The dependence of the rate of thickening on the orientation of individual crystallites of soft plates was not a disturbing factor.

Action of Air on Metals

Colors, which are associated with the formation of thin oxide coatings, occur upon heating of Fe, Co, Ni, Mn, Cr, Cu, Sb, Bi, Sn, Pb, Zn, and Cd. At room temperatures Tl assumes colors; Al shows no colors.

In the tests with air, no particular importance need be attached to the variable flow velocity of the gas since the thickening velocity was found to be independent of it.

As far as investigated, the time-thickness curves due to the oxidation of the metals were, without exception, obtained as exponential curves.

Iron

The colors of iron (electrolytic iron) are bright to light blue and suitable for measurements. Those of the higher orders were recognizable but were weakened by a grey undertone in such manner that they could not be easily distinguished.

A strong dependence of the appearance of the colors on the oxygen content of the oxygen-nitrogen mixtures was to be expected. It was found, however, that at 331° C within the experimental error there was no change in the appearance of the colors with time in pure oxygen, in air, and in nitrogen-oxygen mixtures with 6, 1.7 and 0.5 volume percent of oxygen.

At 331° C and at various N₂-O₂ mixtures, the colors obtained for Fe were found to be those given in table 9. The last column contains the times computed with $a = 0.00097$ and $b = 2.56$. It is seen that for all O₂ concentrations the obtained times deviate from those computed with the equal a and b values only within the experimental error.

The dependence of the air layers in micromicrons, which correspond to the colors, is shown in figure 5 as a function of $\log t$ for different temperatures in air. The given temperatures are probably all too low by 10°C .

The constant b changes with the temperature, as shown in table 10. The values of the constant b , which gives the tangent of the angle which the logarithmic straight line makes with the y -axis, are determined for 100 micromicrons as unit thickness. In order to obtain the value for 1 micromicron, the given values are to be divided by 100.

If $\log b$ is plotted as a function of the temperature, two straight lines which intersect at 317°C are obtained. The equation which represents b as a function of the temperature from the melting point of iron to 317°C is

$$b = 46 e^{-0.00867(T-273)}$$

and the equation which holds above 317°C is

$$b = 2.81 e^{-0.00479(T - [273 + 317^\circ])}$$

Nickel

Oxidizing with greater difficulty than Fe is Ni. At 350°C after 3 hours in the air stream, it assumes a weak yellow color. The present investigation extends over the temperature range from 400° to 620°C . Showing very bright colors of all orders; the first colors of Ni up to blue resemble those of Fe. The thickness of the equivalent air layers for Ni in air as a function of $\log t$ is shown in figure 6. These straight lines all intersect at the same value of $\log a$. The value of a is 0.0180 ± 0.0004 minute. Values of b as a function of the temperature are shown in table 11.

They may be computed by the equation

$$b = 4.00 e^{-0.00654(T - [273 + 400])}$$

The effect of the oxygen content in $\text{N}_2\text{-O}_2$ mixtures is as follows: From 100 to 20 percent, the oxygen content has an infinitely small effect on the rate of thickening. At 6 percent O_2 , the rate of thickening is appreciably decreased and with further decrease in the O_2 content

it continues to decrease slowly but appreciably. In table 12 the thicknesses of the equivalent air layers for 540° C are given for different N₂-O₂ mixtures from which the effect of the O₂ concentration can be seen.

Copper

After the scale of the colors¹ is passed through, the copper is covered with a dark reddish-brown layer which soon changes into a pure black and easily separates from the copper. At 100° C the action of air on copper becomes appreciable. In table 13 are given the obtained and computed thicknesses of the equivalent air layers for the action of oxygen-nitrogen mixtures for 260° C.

The oxidation velocity of Cu differs in many ways from that of Fe and Ni. Whereas for Fe the oxidation velocity does not depend on the partial pressure of the O₂ within wide limits, it does depend on the partial pressure in the case of Cu. The data of table 13 are plotted in figure 7.

Although, as was to be expected, the initial velocities in N₂-O₂ mixtures decrease with decreasing O₂ content (see table 13) the later velocities unexpectedly increase in reverse sequence. The oxidation velocity of Cu in N₂-O₂ mixtures thus increases with decreasing O₂ content, a fact which was already pointed out in reference 4 as well as in reference 5.

The curves for O₂ can be represented by the normal exponential functions, whereas those curves for the mixtures poorer in O₂ can be represented by this law in later portions only. In their initial portions they show a strong retardation. This retardation in the case of the mixtures poorer in O₂ occurs above 208° C. The values of *a* and *b*, which hold above 208° C, are therefore computed only from the observations which correspond to the colors higher than brownish yellow.

For the isotherms of different temperatures, particular values of *a* hold depending on the O₂ content of the N₂-O₂ mixture. These values of *a* are collected below and next to them are given the number of the observed isotherms which intersect at the corresponding value of *a*.

¹The colors of Cu differ from those of the grey metals because of the natural color of Cu. R. Lowenherz (reference 3) has described these colors more accurately than the Rollet table.

O ₂ content (percent)	a	Number of isotherms
100	0.00080 ± 0.00009	6
50	.014	1
20	.050 ± .008	14
12.5	.068 .003	4

The b values obtained from the isotherms for O₂ and air are presented in table 14.

The $\log b$ as a function of the temperature for the action of oxygen is represented by two straight lines which intersect at 208° C. The equations of the b -values which correspond to these straight lines are:

$$b = 13.1 e^{-0.00892(T-273)}$$

$$b = 2.0 e^{-0.00530(T - [273 + 208^\circ])}$$

For the action of air the values of $\log b$ are likewise represented by two straight lines which would intersect at 168° (fig. 8). A discontinuity occurs, however, at 205° to 220° C. The equation which gives the dependence of b on the temperature from the melting point of iron up to 205° C is

$$b = 24.8 e^{-0.0150(T-273)}$$

above 220° C, the equation is

$$b = 1.20 e^{-0.0105(T - [273 + 220])}$$

A second test series again gave for $\log b$ two straight lines which, however, did not quite coincide with those first determined, but ran almost parallel to them and between 190° and 220° there were several almost equal values of b .

With regard to the phenomenon of retardation which is observed above 208° C, and which is described in more detail by the curves

referring to the mixtures poorer in O_2 , the following is to be said. The plates are colored rather slowly in the O_2 poorer mixtures up to approximately brownish yellow (230 to 245 μ) until the rate of thickness increase at one or more points suddenly rises. These regions are rapidly extended so that after a few seconds the plates appear uniformly colored. The same retardation phenomenon was observed above $208^\circ C$ if the plate was not exposed a sufficiently long time to a pure O_2 atmosphere before it was placed in the heating tube.

In order to explain the retardations in the initial stage of the oxidation above $208^\circ C$, it may be assumed that an oxide body is formed for whose formation the presence of nitrogen is required; this differs from the two other oxides, which correspond to the two straight lines representing the value of $\log b$ as a function of the temperature, in that it possesses a much smaller penetrability for oxygen than the other two oxides. If this body is unstable and easily passes over into one of the other oxides, this previous observation is understandable; namely, starting from the color brown-yellow at individual points, the higher colors are very rapidly formed and quickly spread over the entire plate. The assumption of a conversion of the first oxide into the second is not admissible for explaining the retardation above $208^\circ C$ because the first oxide would require a more rapid initial velocity than the second if it were producible at this temperature. The cause of the retardation cannot likewise be sought in a nitrogen layer absorbed by the Cu because this phenomenon was not observed below $208^\circ C$.

Zinc, Cadmium, Tin, Lead, Cobalt, and Manganese

The Zn and Cd show rather dull colors; Sn and Pb very bright colors. In the case of Sn and Pb, the action of the liquid metal was likewise observed. Since the velocity depends only on the diffusion of the oxygen through the oxide coating, no change in the direction of the straight lines, which represent the dependence of the values of $\log b$ on the temperature, was to be expected. In the case of Pb, the values of $\log b$ actually lie approximately on a straight line. In the case of Sn, however, the dependence is represented by two straight lines which intersect at the melting point of the Sn. The constant a has the same value for the crystallized and the liquid metal.

Tables 15 to 18 give the air thicknesses, corresponding to the colors, and the corresponding a and b values.

For Co and Mn the values of a and b were obtained as shown in tables 15 to 18.

Summary of Results on Oxidation Rate of Metals

1. The oxide layers increase in thickness with time according to the exponential law of equation (3). The constant a was found, in general, to be independent of the temperature and the constant b depends on the temperature according to the given exponential law.

2. The process of the oxidation is determined by the diffusion of the oxidizing agent through the oxide layers. The composition of these layers is, in general, unknown. If the metal forms only a single oxide the formation of the oxide is naturally very simple; if, however, several oxides can be formed the oxygen pressure of which is smaller than the partial pressure of the oxygen in the gas mixture, some doubt may exist as to the types of oxide formed.

If the $\log b$ can be represented as a function of the temperature by a straight line, it is very probable that at the temperature interval considered, only a single oxide is formed. In the case of Zn, Cd, Ni, and Pb a single oxide is formed for dry oxidation and for these metals $\log b$ as a function of the temperature is represented by a straight line, whereas for Cu and Fe the dependence is represented in each case by two intersecting lines. From this it is not to be concluded, however, that in the case of Cu one straight line corresponds to the formation of Cu_2O and the other to CuO . For, in the formation of thick oxide layers on Cu itself, Cu_2O always occurs as a macroscopic layer. The two straight lines of $\log b$ can therefore only correspond to the two different forms of Cu_2O and from the described abnormality of the Cu action, above 208°C there would be probably the existence of either a third unstable form of the Cu_2O or an oxide of another composition.

3. The dependence of the initial velocity on the oxygen content of the acting gas mixture gives information on the process of the oxidation itself. In table 19, these values are given for Cu, Ni, and Fe.

For Cu the initial velocity for an oxygen content smaller than 50 percent is approximately proportional to the oxygen content. This would indicate that, in this case, the oxygen molecule as such acts as the oxidizer. In pure oxygen, however, the initial velocity is very much greater than would be expected from this proportionality. For Ni the number of observations is insufficient to determine the dependence of the initial velocity on the oxygen content in general. For Fe the initial velocity is independent of the oxygen content. This independence is a phenomenon that is very difficult to understand. It recalls the independence of the oxidation velocity of phosphorus for oxygen pressures between 100 and 500 millimeters.

The production of pure metal surfaces was attempted, in order to show that for dry air, no change in the surface was produced even for long times. The Zn, Cd, and Pb were melted in a dry hydrogen stream and by inclining the test, apparatus parts of the melt were freed from the oxygen coating. After cooling in the hydrogen stream, the blank surfaces of these pieces, after they were melted over P_2O_5 , showed, under a green light, a violet color, which, however, could not be seen under a white light. Evidently, very small amounts of oxygen and hydrogen vapor were sufficient to produce this violet color. After this coating was formed it remained unchanged for 3 months. The production of pure surfaces of metals as in the production of photoelectric cells is thus possible only in a vacuum.

4. From the variation of the thickness of the oxide layers at higher temperatures, information may be obtained on this variation at lower temperatures with the aid of the given equations. The exponential equations for b as a function of the temperature make possible the extrapolation of b to ordinary temperature ($15^\circ C$) and, since a was found to be independent of the temperature, the time could be computed after which at $15^\circ C$ an oxide layer is formed that gives rise to a definite color. In table 20 the times are computed in years, after which the first appreciable visible color is produced on the various metals, the first yellow, in dry air. To the first yellow, there corresponds an air layer of 164 micromicrons; dividing this value by the index of refraction of the corresponding oxide, yields the thickness of the oxide layer, which corresponds to the first yellow.

There is also given in the table the initial velocities $1/ab$ in micromicrons per minute for $15^\circ C$. If the oxide coat would not hinder the action of the oxygen, the Fe would in 1 minute pass through all the clearly visible colors and the first yellow would similarly appear on the Cu after 1 minute. In spite of this high initial velocity, it takes an extremely long time until the first yellow would be observed at $15^\circ C$.

In the third column is given the time in seconds, to which corresponds an air-layer thickness of 14.10^{-7} millimeters. This time would correspond approximately to the formation of the space lattice of the oxide.

From the tests at high temperature it is to be concluded that the metals with the exception of the nonoxidizable ones are almost instantaneously covered with an oxide coating, which, although very thin, so well protects the metals from the oxidation that further oxidation becomes unobservable. In dry air the metals at $15^\circ C$ should not show any colors even after many years, a fact which agrees with experience.

In vapor-containing air, the change in the metals proceeds much more rapidly than in dry air; the dry oxidation is not to be confused with wet oxidation.

Action of Air on Cu-Zn Alloys

At 115° C these alloys in the soft state were exposed to the air and after various times their colors were determined. The equivalent air-layer thicknesses as a function of the time are exponential curves, whose a-values from 0 to 70 percent Cu lie between 0.05 and 0.06, while those of 30 to 100 percent Cu lie at 0.01. The b-values increase at a particularly great rate for the β - and γ -mixture crystals. For these curves the times were taken to which corresponded the color of the equivalent air layer 300 micromicrons. These times are plotted in figure 9 as a function of the Cu content of the alloys.

The velocity on differently orientated intersection planes through the crystallite is very different, corresponding to several different times for the same Cu content of figure 9. This difference is observable for 80 percent Cu and assumes the greatest values in the case of the β - and γ -mixture crystals, as is seen in figure 9. For the crystallites of the β - and γ -mixture crystals, there are also intersection planes, however, for which the times taken to attain the thickness 300 micromicrons were so large that it was impossible to wait until it was attained. For the ϵ - and η -mixture crystals, these differences vanish.

The time for attaining the thickness 300 micromicrons of Zn is considerably greater than that of Cu. With increasing Zn content these times increase and, for the β - and γ -mixture crystals, for certain surfaces attain the Zn value, whereas for other surfaces the Zn value is far exceeded. The diffusion of the oxygen through the Cu_2O and ZnO containing coatings on certain planes of the β and γ -mixture crystals is thus more strongly hindered than through these coatings on other planes on which this diffusion velocity attains values which correspond to ZnO . For the β - and γ -mixture crystals, these differences are particularly large, very much greater than on differently oriented planes of pure metals.

For pure metals too, after particularly careful polishing, different colors occur on different crystallites because the anisotropic layers of the reaction products are oriented in a definite manner to the various crystallite planes and because the diffusion velocity is a vectorial property.

The occurrence of a homogeneous cohering layer and the dependence of its orientation on the plane on which it is formed indicate a par-

ticularly regular reaction phenomenon. If on a lattice plane of the metal analogous distances of the metal atoms were half as large as those of the metal atoms at the same lattice plane of the reaction product, its formation could proceed in the manner shown in figure 10. On the incidence of the molecules of the reagent (Cl_2) (circles) its atoms interchange with alternating atoms (crosses) of the lattice line ab, and the alternating atoms jump into a lattice line cd of the reaction product, and form, with the remaining atoms of the reagent, a second lattice line of the reaction product. In this manner, a lattice line of the metal would be converted into two of the reaction product. The condition for such a regular reaction process will not correspond to the lattice parameters of the metal and its reaction product on equal lattice planes of the two. In order, however, that a regular reaction process occur, a lattice plane of the reaction product must be formed, which of all others, most nearly corresponds to this condition. The exact satisfying of this extended condition will, in general, be impossible if it is required in the strict sense for a lattice plane but will be possible if the concept of the lattice plane is replaced by that of a layer of minimum thickness. It is then possible, from all the lattice plane layers of the lattice of the reaction product, to choose that pair whose projected metal atoms on the middle plane are at distances from each other which are equal to those of the atoms in the metal lattice. The layer thickness of this pair should be the minimum. Through the satisfying of this condition, the orientation of the layer relative to the orientation of the metal crystal would be determined. The lattice plane of the reaction product will vary with the lattice plane of the metal crystal, and with it the penetrability for the reagent and therefore the rate of thickness increase.

Translated by S. Reiss
National Advisory Committee
for Aeronautics.

REFERENCES

1. Z. anorg. u. allg. Chem. 111, 1920, 78.
2. Landolts Tabellen, 1905, tab, 186, p. 610.
3. Löwenherz, R.: Z. F. Instrumentenkunde, 1889, p. 316.
4. Müller, W. Pogg. Ann. 141, 1870, 95.
5. Jordis, E., and Rosenhaupt, W.: Z. angew. Chem. 21, 1908, 55.

TABLE 9 - IRON IN N₂-O₂ MIXTURES

O ₂ content (percent)	100	20	6	1.75	0.5	
μ	sec obtained					sec computed
164	7	8	8	7	8	5
235	20	20	20	22	30	25
245	28	30	30	30	35	32
257	45	43	50	40	45	45
272	70	60	60	55	60	66
282	95	90	105	90	85	85
300	135	135	135	135	135	135

TABLE 10 - b FOR Fe IN AIR

Temperature	b obtained	b computed	Temperature	b obtained	b computed
252	4.84	4.95	328	2.64	2.66
270	4.31	4.26	335	2.57	2.57
275	4.03	4.08	345	2.41	2.45
290	3.68	3.58	350	2.34	2.40
305	3.18	3.15	357	2.35	2.34
307	3.05	3.07	366	2.22	2.22
317	2.81	2.81	385	2.05	2.05
---	----	----	404	1.90	1.87

TABLE 11 - b FOR Ni IN AIR

Temperature	b obtained	b computed
425	3.09	3.35
485	2.34	2.34
515	1.95	1.95
543	1.65	1.64
559	1.50	1.49
575	1.34	1.35
595	1.22	1.20
620	1.03	1.03
645	.83	.88

TABLE 12 - NI IN N₂-O₂ MIXTURES

O ₂ content (percent)	100		20		6.5		1.4		0.5	
μμ obtained	min.	μμ com- puted	min.	μμ com- puted	min.	μμ com- puted	min.	μμ com- puted	min.	μμ com- puted
245	0.16	220	0.20	220	0.20	230	----	---	0.58	255
272	.25	260	.25	240	.33	264	0.50	268	----	---
282	.33	282	.42	285	.50	288	.66	286	1.00	284
300	.42	308	.50	302	.66	305	.92	306	1.33	300
352	.60	344	.75	342	1.25	348	2.00	352	3.00	344
387	.85	375	1.25	387	2.50	390	3.75	392	7.00	390
409	1.25	409	1.50	404	3.00	404	5.00	410	12.00	415
435	1.50	432	2.20	432	4.50	430	7.00	434	-----	---
465	2.25	465	2.75	460	8.00	468	9.00	450	-----	---
490	2.75	488	3.75	488	10.00	484	-----	---	-----	---
520	3.75	518	5.00	516	-----	---	-----	---	-----	---
540°	a = 0.0177 b = 1.05		a = 0.0177 b = 1.09		a = 0.0058 b = 11.52		a = 0.0058 b = 1.61		a = 0.0058 b = 1.81	

TABLE 13 - Cu IN N₂-O₂ MIXTURES

Oxygen, Percent

100			50			20			12.5		
min.	μμ		min.	μμ		min.	μμ		min.	μμ	
	ob- tained	com- puted		ob- tained	com- puted		ob- tained	com- puted		ob- tained	com- puted
0.25	300	330	0.33	245	255	0.5	164	280	1	164	380
.5	372	375	.5	300	324	1	245	370	1.5	257	435
1.25	435	430	.75	372	365	1.25	300	400	2.25	490	490
2	465	458	1	387	392	1.5	387	420	2.75	520	524
3.5	490	490	1.5	435	428	1.75	435	438	3.5	550	552
6	520	520	2	465	456	2.25	465	467	4.25	570	576
8.5	550	540	2.5	490	478	2.5	490	484	5	600	604
13	570	568	4	520	520	3.5	520	525	7	650	644
17.5	600	588	5	550	540	4.25	550	550	9	670	680
-----	---	---	7	570	570	5	570	570	13	720	730
-----	---	---	9.5	600	596	6	600	592	-----	---	---
-----	---	---	16	655	644	9	650	640	-----	---	---

TABLE 14 - b FOR Cu IN O₂ AND AIR

O ₂			Air			Air	
Temper- ature	b obtained	b computed	Temper- ature	b obtained	b computed	Temper- ature	b
---	----	----	134	3.37	3.39	---	----
175	2.70	2.70	140	3.03	3.10	154	2.19
187	2.40	2.42	160	2.35	2.30	165	1.95
200	2.18	2.18	172	1.95	1.96	190	1.39
218	1.90	1.90	190	1.50	1.50	197	1.36
230	1.78	1.78	205	1.24	1.24	210	1.36
250	1.60	1.59	220	1.16	1.20	224	1.32
---	----	----	227	1.12	1.12	260	.92
---	----	----	231	1.10	1.08	---	----
---	----	----	245	.94	.93	---	----
---	----	----	256	.81	.82	---	----
---	----	----	262	.78	.78	---	----
---	----	----	272	.69	.69	---	----
---	----	----	305	.49	.49	---	----

TABLE 15 - Zn IN AIR

390°			412°			a = 0.0660 ± 0.0025		
min.	μ		min.	μ		Temper- ature	b obtained	b computed
	ob- tained	com- puted		ob- tained	com- puted			
0.5	164	160	0.5	164	175	---	----	----
1.5	245	245	1.2	245	257	375	1.38	1.38
2	272	268	2	300	300	390	1.25	1.26
3	300	300	4	352	365	412	1.09	1.09
5	352	342	8	435	435	---	----	----
9	387	382	10	465	450	---	----	----
12	409	412	----	---	---	---	----	----
14.5	435	430	----	---	---	---	----	----

TABLE 16 - Cd IN AIR

290°			315°			a = 0.0055 ± 0.0004		
min.	μμ		min.	μμ		Temper- ature	b obtained	b computed
	ob- tained	com- puted		ob- tained	com- puted			
0.16	164	160	0.33	245	232	---	----	----
.75	245	240	.66	272	272	315	1.79	1.81
1.3	257	242	1	300	296	307	1.95	1.96
2	282	280	4	352	364	300	2.05	2.05
3	300	300	8	409	415	290	2.19	2.22
10	352	352	12	435	438	257	2.83	2.86
-----	---	---	19	465	465	---	----	----

TABLE 17 - Sn IN AIR

224°			400°			a = 0.0060 ± 0.0006					
min.	μμ		min.	μμ		Static			Dynamic		
	ob- tained	com- puted		ob- tained	com- puted	Tem- pera- ture	b ob- tained	b com- puted	Tem- pera- ture	b ob- tained	b com- puted
1	164	168	0.5	245	240	195	3.97	4.00	260	3.00	2.60
6	235	230	1	282	280	200	3.79	3.81	320	2.56	2.22
9.5	245	245	1.5	300	305	206	3.61	3.60	330	2.60	2.18
14	257	260	3	352	340	218	3.19	3.19	345	2.10	2.09
22	272	274	9	387	396	224	2.89	2.96	375	2.00	2.02
27	282	280	16	435	435	225	3.08	2.95	400	1.80	1.80
45	300	300	-----	---	---	---	----	----	420	1.70	1.68

TABLE 18 - Pb IN AIR

290°			315°			a = 0.035 ± 0.006					
min.	μμ		min.	μμ		Static			Dynamic		
	ob- tained	com- puted		ob- tained	com- puted	Tem- pera- ture	b ob- tained	b com- puted	Tem- pera- ture	b ob- tained	b com- puted
0.5	164	168	0.5	164	180	260	2.29	2.22	355	0.83	0.98
2	245	245	.84	245	230	290	1.60	1.68	415	.69	.62
3	272	275	1.5	272	278	315	1.40	1.36	450	.47	.47
3.75	282	290	2	300	300	325	1.25	1.24	---	----	----
4.5	300	300	3	352	340	---	----	----	---	----	----
8	352	338	4.5	387	376	---	----	----	---	----	----

TABLE 19

Cu 260°			Fe 331°		Ni 331°
(percent)	$\frac{1}{ab}$ $\mu\mu$ per min.	$\frac{1}{ab}$ (per cent)	O ₂ (percent)	$\frac{1}{ab}$ $\mu\mu$ per min.	O ₂ (percent)
100	735300	---	100	} 40,280	100
50	6550	131	20		20
20	2410	120	6		6.5
12.5	1980	158	1.75		1.4
-----	-----	---	.5		.5

TABLE 20

Metal	Year	Initial Velocity	Sec
Pb	90	219	0.42
Zn	31.10 ²	104	.88
Cd	19.10 ⁵	778	.13
Cu	6.10 ⁸	89	1.11
Sn	36.10 ⁸	856	.15
Fe	25.10 ¹⁷	2712	.05
Ni	475.10 ¹⁷	146	.95

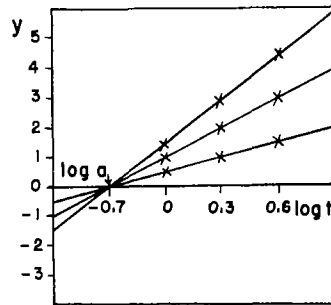


Figure 1.

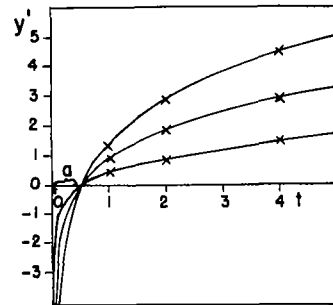


Figure 2.

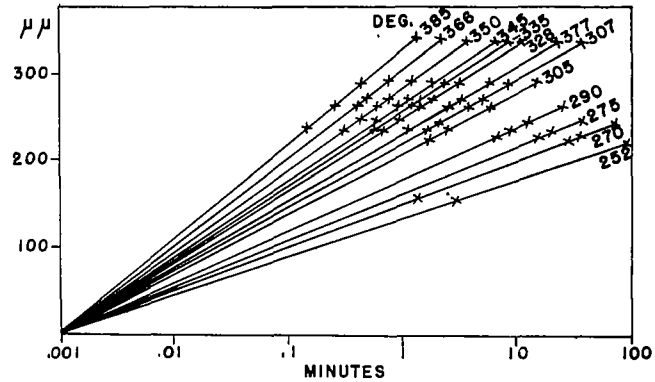


Figure 5.

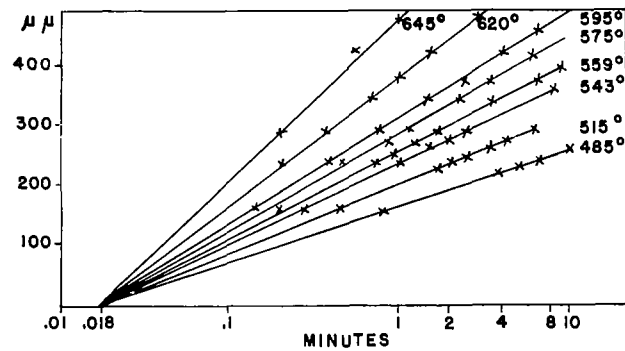


Figure 6.

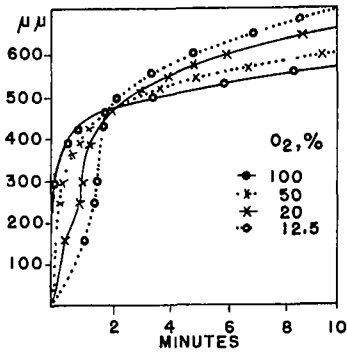


Figure 7.

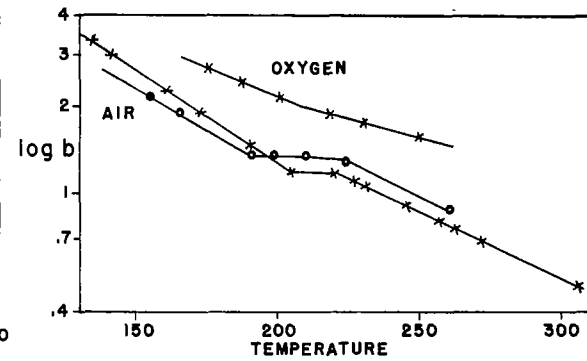


Figure 8.

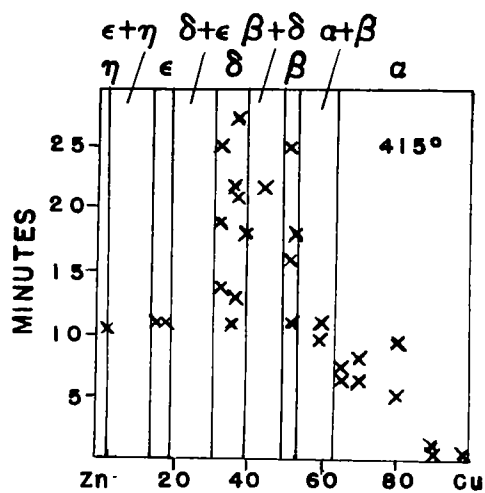


Figure 9.

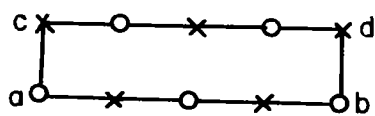


Figure 10.